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# Fast and safe synthesis of micron germanium in an ammonia atmosphere using Mo<sub>2</sub>N as catalyst

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Here, we reported a new method for fast and safe synthesis of a micron germanium (Ge) semiconductor. The Ge was successfully prepared from mixed GeO<sub>2</sub> with a low amount of MoO<sub>3</sub> by the NH<sub>3</sub> reduction method at 800 °C for an ultra-short time of 10 min. XRD patterns show that the Ge has a tetragonal structure. SEM images show that the size of the Ge particles is from 5 μm to 10 μm, and so it is on the micron scale. UV-visible diffuse reflectance spectroscopy shows that the Ge has good light absorption both in the ultraviolet and visible regions. The formation of Ge mainly goes through a two-step conversion in the NH<sub>3</sub> flow. Firstly, GeO<sub>2</sub> is converted to Ge<sub>3</sub>N<sub>4</sub>, and then Ge<sub>3</sub>N<sub>4</sub> is decomposed to generate Ge. The comparison experiments of MoO<sub>3</sub> and Mo<sub>2</sub>N demonstrate that Mo<sub>2</sub>N is the catalyst for the Ge synthesis which improves the Ge<sub>3</sub>N<sub>4</sub> decomposition. The presented fast and safe synthesis method of Ge has great potential for industrialization and the proposed Mo<sub>2</sub>N boosting the Ge<sub>3</sub>N<sub>4</sub> decomposition has provided significant guidance for other nitride decomposition systems.

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## 1 Introduction

With the development of advanced electronic information industries, semiconductor materials have attracted widespread attention due to their unique optical and electrical properties.<sup>1–6</sup> Ge as an important semiconductor material with stable chemical properties and obvious non-metallic properties has many advantages, such as non-toxicity, biocompatibility, electrochemical stability, current microelectronics compatibility, *etc.*<sup>7–13</sup> At present, Ge has extensive and important applications in fields such as semiconductors, aerospace measurement and control, nuclear physics detection, optical fiber communication, infrared optics, solar cells, chemical catalysts, and biomedicine.<sup>14–20</sup> Ge is one of the most dispersed elements and there is almost no concentrated Ge deposit in the Earth's crust. Thus, it is particularly important to find suitable methods to enrich, prepare and purify Ge.

The synthetic method of Ge can be divided into physical and chemical methods. The physical methods mainly include chemical vapor deposition,<sup>21</sup> gas phase pyrolysis,<sup>22</sup> plasma technology,<sup>23–25</sup> sputtering,<sup>26,27</sup> etching,<sup>28,29</sup> laser ablation<sup>30</sup> and so on. However, these technological processes need extreme temperatures and pressures and are expensive. Chemical methods mainly include room temperature reduction of a GeCl<sub>4</sub>/Br<sub>4</sub> precursor,<sup>31,32</sup> high temperature reduction of a GeI<sub>2</sub>/I<sub>4</sub> precursor,<sup>33,34</sup> a one-step synthesis method,<sup>35,36</sup> an electrodeposition method<sup>37–41</sup> and so on. In the industry, rough Ge is

commonly prepared by the reduction of GeO<sub>2</sub> in hydrogen flow at 650–680 °C, and then Ge with high purity is obtained by chemical gasification and decomposition of rough Ge. However, in the process of preparing rough Ge, the produced hydrogen is a dangerous gas due to its large range of the explosion limit. In addition, a leak of hydrogen is not easy to discover due to it being colorless and tasteless. So, it is necessary to develop and improve a safe and low-cost method to produce rough Ge.

Ammonia is an important chemical raw material, which has important applications in industrial and agricultural production. At the same time, ammonia is also a reducing gas capable of reducing various metal oxides.<sup>42–45</sup> Here, we successfully prepared micron Ge material in ammonia atmosphere using GeO<sub>2</sub> as raw material with some MoO<sub>3</sub> in 10 min. The transformation process from GeO<sub>2</sub> to Ge and the molybdenum based catalyst were determined. The synthesis method of Ge has the advantages of safe, fast and low cost, which is beneficial to industrial production.

## 2 Experimental

### 2.1 Synthesis of Ge

All the chemical agents are from China National Pharmaceutical Group Corporation. GeO<sub>2</sub> as raw material and a small amount of MoO<sub>3</sub> are mixed and milled in a mortar for 30 minutes. The mixed samples are calcined in an ammonia flow of 100 mL min<sup>-1</sup> at different temperature and for different time. The synthesis of Ge in H<sub>2</sub> flow is same as that in NH<sub>3</sub> flow except H<sub>2</sub> instead of NH<sub>3</sub>.

Also, in this paper A/B means A mixed with B. For example, Mo<sub>2</sub>N/GeO<sub>2</sub> means Mo<sub>2</sub>N mixed with GeO<sub>2</sub>.

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## 2.2 Characterization

The structure of the as-prepared Ge was determined by X-ray diffraction (D/MAX2500, Rigaku, Japan) with a Cu-K $\alpha$  radiation at a voltage of 4 kV at room temperature. The ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) were obtained on a spectrometer (U-4100), and BaSO $_4$  was used for the corrected base line. The size and morphology were examined by scanning electron microscopy (SEM, JSM7500F) with the accelerating voltage of 0.5–30 kV and transmission electron microscopy (TEM, F20) with the accelerating voltage of 120 kV.

## 3 Results and discussion

### 3.1 Synthesis of Ge in NH $_3$ flow using Mo based catalyst

Fig. 1 shows the XRD patterns of GeO $_2$  calcined at different temperatures in an ammonia atmosphere. The XRD of the GeO $_2$  is also present for comparison. When the reaction temperature is lower than 800 °C, GeO $_2$  (PDF # 36-1463) still remain unchanged. At 800 °C, all GeO $_2$  changed into Ge $_3$ N $_4$  (PDF # 38-1374). At 900 °C, a part of Ge (PDF # 04-0545,  $2\theta = 27.5^\circ$ ) generates which indicates a small part of Ge $_3$ N $_4$  decomposes at overhigh temperature.

Fig. 2 shows the XRD patterns of 5.0 wt% MoO $_3$ /GeO $_2$  calcined in NH $_3$  flow at different temperatures for 2 h. It can be seen that when the reaction temperature is at or above 800 °C, almost all the GeO $_2$  are changed into Ge (PDF # 04-0545). Comparing with Fig. 1, the introduction of the Mo element decreases the reaction temperature of Ge generation over 100 °C.

Fig. 3 shows XRD patterns of 5.0 wt% MoO $_3$ /GeO $_2$  calcined in NH $_3$  flow at 800 °C for different time. The process of Ge generation is ultra fast and almost all the GeO $_2$  can be reduced to Ge in 10 min. Fig. 4 shows the XRD pattern of MoO $_3$ /GeO $_2$  with different mass ratio calcined in ammonia flow. When the amount of MoO $_3$  is less than 5.0%, the reaction product is Ge and Ge $_3$ N $_4$  (e.g. the sample of 2.0 wt% MoO $_3$ /GeO $_2$ ). When the amount of MoO $_3$  is 5.0%, almost all the GeO $_2$  is converted to Ge. In view of the fact of that GeO $_2$  changed into Ge $_3$ N $_4$  (Fig. 1, 800

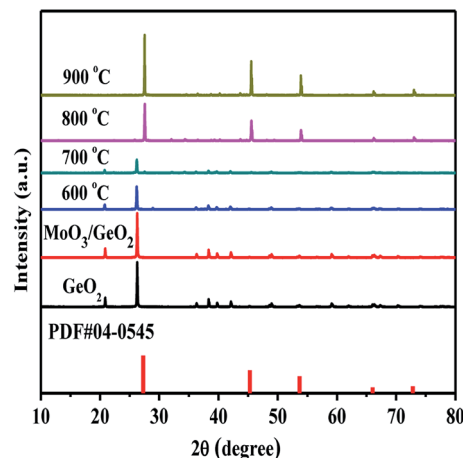


Fig. 2 XRD patterns of commercial GeO $_2$  and samples of 5.0 wt% MoO $_3$ /GeO $_2$  calcined in NH $_3$  flow at different temperatures for 2 h.

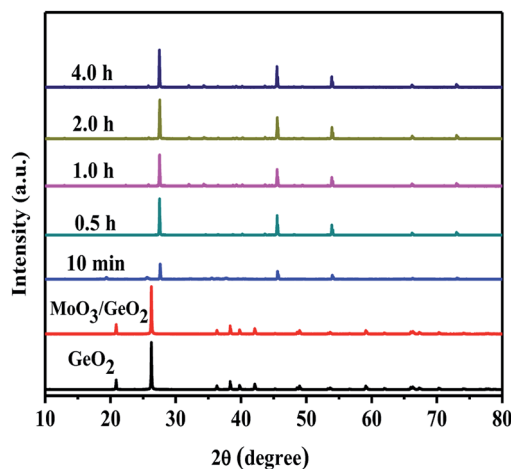


Fig. 3 XRD patterns of commercial GeO $_2$ , 5.0 wt% MoO $_3$ /GeO $_2$  and 5.0 wt% MoO $_3$ /GeO $_2$  calcined in NH $_3$  flow at 800 °C for different time.

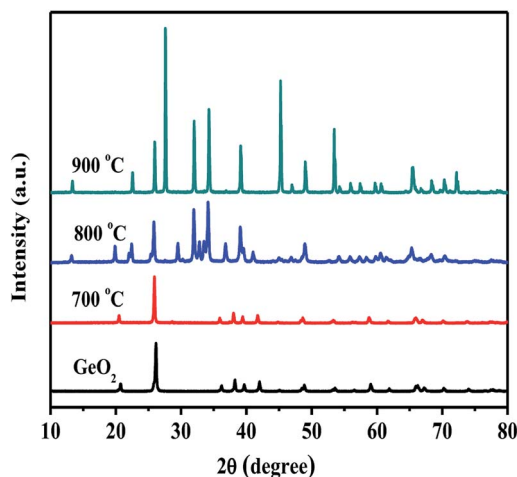


Fig. 1 XRD patterns of commercial GeO $_2$  and GeO $_2$  calcined in NH $_3$  flow at different temperatures for 2 h.

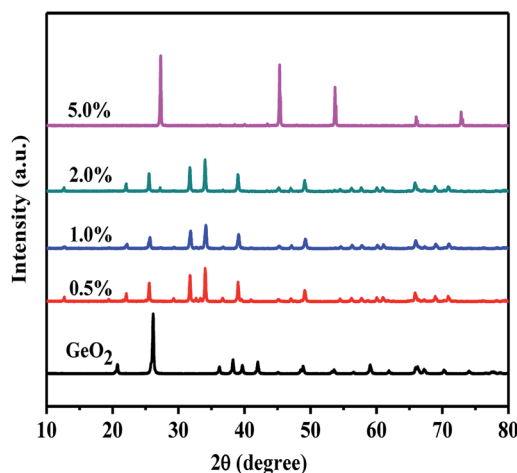


Fig. 4 XRD patterns of GeO $_2$  and MoO $_3$ /GeO $_2$  with different MoO $_3$  loading mass ratio calcined in NH $_3$  flow at 800 °C for 0.5 h.



°C) without any catalyst, we inferred the process Ge generation is that first the  $\text{GeO}_2$  transfers into  $\text{Ge}_3\text{N}_4$ , and then the  $\text{Ge}_3\text{N}_4$  decomposes into Ge with the Mo base catalyst. This ultra fast method of Ge generation using Mo based catalyst has major advantages of low cost and high efficiency.

### 3.2 Determination of the catalyst of Ge generation

It is well known the molybdenum oxide will change into molybdenum nitride in  $\text{NH}_3$  atmosphere at high temperature. So, it is necessary to judge which Mo species play the catalytic role in the Ge generation. Fig. 5 shows XRD patterns of  $\text{MoO}_3$  calcined in the  $\text{NH}_3$  flow at different temperatures. At 600 °C, some  $\text{MoO}_3$  (PDF # 35-0609) is reduced into  $\text{MoO}_2$  (PDF # 32-0671). When the temperatures reach at and above 700 °C, all  $\text{MoO}_3$  is converted to  $\text{Mo}_2\text{N}$  (PDF # 25-1366). In Fig. 2, Ge is generated at 800 °C from  $\text{MoO}_3/\text{GeO}_2$ . At this moment (800 °C), the  $\text{MoO}_3$  had been reduced into  $\text{Mo}_2\text{N}$  (Fig. 5, 800 °C), and the  $\text{GeO}_2$  had been reduced into  $\text{Ge}_3\text{N}_4$  (Fig. 1, 800 °C). These results indicate that the  $\text{Mo}_2\text{N}$  generated by  $\text{MoO}_3$  acts as a catalyst and improves the decomposition of the  $\text{Ge}_3\text{N}_4$  into Ge.

In order further determine the origination ( $\text{Mo}_2\text{N}$  or  $\text{MoO}_3$ ) of the catalysis role in Ge generation, the calcination experiments in nitrogen flow using  $\text{GeO}_2$  and  $\text{Ge}_3\text{N}_4$  as raw materials have been designed. Fig. 6 shows the XRD patterns of  $\text{Mo}_2\text{N}/\text{GeO}_2$ ,  $\text{MoO}_3/\text{GeO}_2$ ,  $\text{Mo}_2\text{N}/\text{Ge}_3\text{N}_4$  and  $\text{MoO}_3/\text{Ge}_3\text{N}_4$  calcined in  $\text{N}_2$  atmosphere at 800 °C for 2 h. It can be seen that there are all a small amount of Ge generated by the addition of  $\text{Mo}_2\text{N}$  whether the raw material is  $\text{GeO}_2$  or  $\text{Ge}_3\text{N}_4$ . However, by the addition of  $\text{MoO}_3$ , there is no Ge generation for both  $\text{MoO}_3/\text{GeO}_2$  and  $\text{MoO}_3/\text{Ge}_3\text{N}_4$ . These again demonstrate that  $\text{Mo}_2\text{N}$  plays the catalysis role in Ge generation, whereas  $\text{MoO}_3$  is not the catalyst.

### 3.3 Comparison with the industrial preparation method of Ge in $\text{H}_2$ flow

In order to compare our preparation method with industrial method,  $\text{GeO}_2$  is reduced into Ge in hydrogen atmosphere has been carried out. Fig. 7 shows the XRD patterns of  $\text{GeO}_2$  calcined in hydrogen flow at different temperatures for 4 hours. At or over 500 °C, Ge is generated in  $\text{H}_2$  flow, and 650 °C is

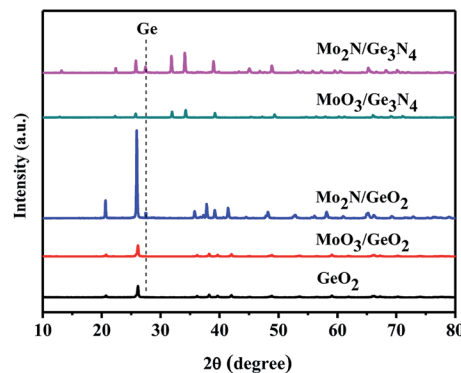


Fig. 6 XRD patterns of  $\text{GeO}_2$ , 5.0%  $\text{Mo}_2\text{N}/\text{GeO}_2$ , 5.0%  $\text{MoO}_3/\text{GeO}_2$ , 5.0%  $\text{Mo}_2\text{N}/\text{Ge}_3\text{N}_4$  and 5.0%  $\text{MoO}_3/\text{Ge}_3\text{N}_4$  calcined in  $\text{N}_2$  atmosphere at 800 °C for 2 h.

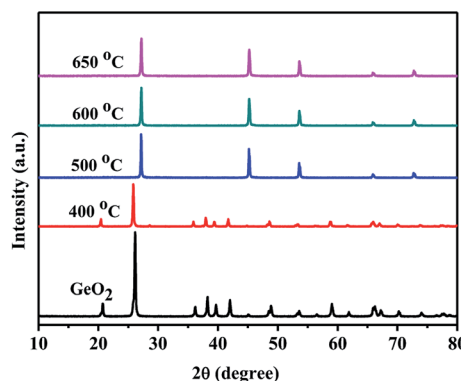


Fig. 7 XRD patterns of  $\text{GeO}_2$  calcined in hydrogen atmosphere at different temperatures for 4 h.

chosen generally in the industry. Fig. 8 shows the XRD pattern of  $\text{GeO}_2$  calcined in hydrogen flow at 500 °C for different time. Ge can be produced in the  $\text{H}_2$  flow in 2 hours. So, compared with the industrial method in the  $\text{H}_2$  flow, our preparation method in the  $\text{NH}_3$  flow with  $\text{Mo}_2\text{N}$  catalyst has the advantages of ultra short reaction time (10 min vs. 2 h) and more safety ( $\text{NH}_3$  vs.  $\text{H}_2$ ), though the reaction temperature is higher (800 °C

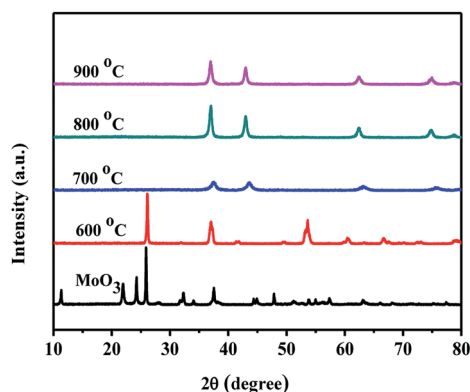


Fig. 5 XRD patterns of  $\text{MoO}_3$  and  $\text{MoO}_3$  calcined in  $\text{NH}_3$  flow at different temperatures for 2 h.

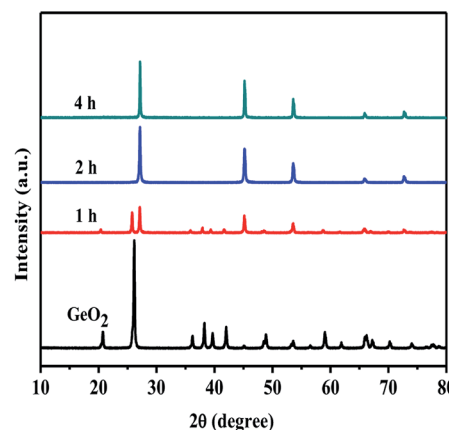


Fig. 8 XRD patterns of  $\text{GeO}_2$  calcined in  $\text{H}_2$  flow at 500 °C for different time.



vs. 650 °C). We also performed the experiment which the GeO<sub>2</sub> was calcined in H<sub>2</sub> flow at 800 °C for the further contrast. The Fig. 9 shows the XRD pattern of GeO<sub>2</sub> calcined in hydrogen flow at 800 °C for different time. The GeO<sub>2</sub> was converted into Ge in 10 min under the hydrogen atmosphere at 800 °C. It is similar to that of in the NH<sub>3</sub> flow reduction. However, calcining GeO<sub>2</sub> in an ammonia atmosphere means more secure.

### 3.4 The physical properties of prepared Ge

Fig. 10 shows the morphologies of the raw material GeO<sub>2</sub> and the prepared Ge in NH<sub>3</sub> flow with different magnifications. The GeO<sub>2</sub> particles (Fig. 10a–c) are uniform and show sharp angular shapes. The prepared Ge in NH<sub>3</sub> flow (Fig. 10d–f) shows a smooth surface and some agglomeration, indicating the structure changes from GeO<sub>2</sub> to Ge. The size of Ge is between 5 μm and 10 μm. Fig. 11 shows the HRTEM of prepared Ge in NH<sub>3</sub> flow, the lattice fringes of Ge with interplanar distances of 0.237 nm is indexed to the (111) planes of Ge.

In order to further explore the morphology changes in the formation process of Ge, SEM as shown in Fig. 12 has been carried out for the samples prepared from MoO<sub>3</sub>/GeO<sub>2</sub> for different times and with different MoO<sub>3</sub> mass ratios. Compared the Fig. 12b with Fig. 12a, it is found the rod-shaped material

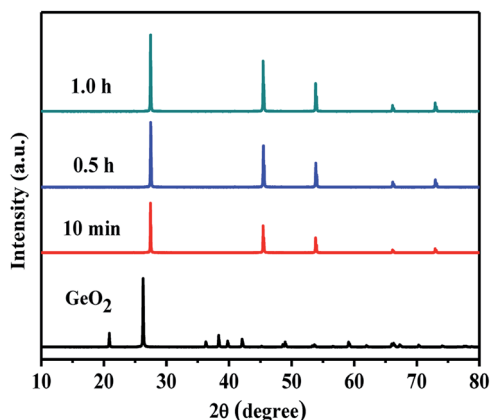


Fig. 9 XRD patterns of GeO<sub>2</sub> calcined in H<sub>2</sub> flow at 800 °C for different time.

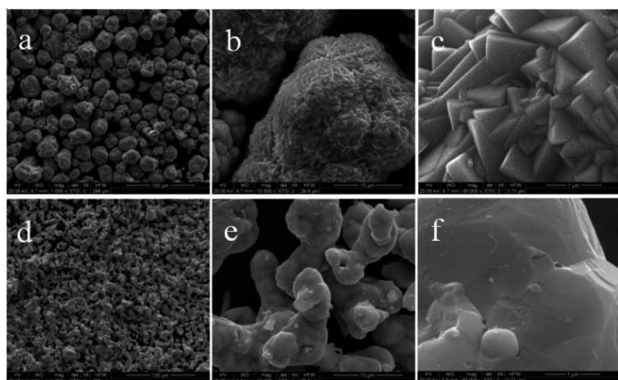


Fig. 10 SEM images of the raw material of GeO<sub>2</sub> (a–c) and the Ge (d–f) prepared from 5% MoO<sub>3</sub>/GeO<sub>2</sub> in NH<sub>3</sub> flow at 800 °C for 2 h.

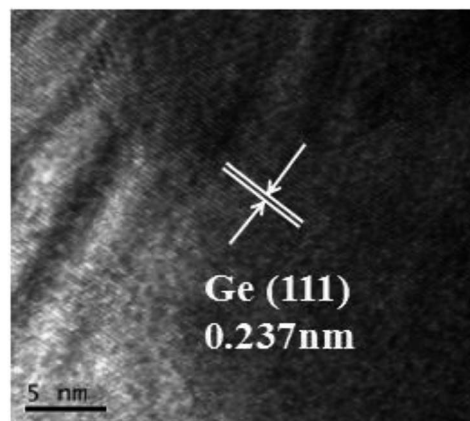


Fig. 11 HRTEM of Ge prepared in the NH<sub>3</sub> flow from GeO<sub>2</sub> mixed with 5.0% MoO<sub>3</sub> at 800 °C for 2 h.

(Fig. 12a) decreases and the large smooth-surfaced Ge (Fig. 12b) increases with the reaction time prolonging. Associate with XRD patterns in Fig. 4, the rod-shaped material can be inferred as Ge<sub>3</sub>N<sub>4</sub>. Compared the Fig. 12c with Fig. 12b, it can be seen that there is hardly any Ge<sub>3</sub>N<sub>4</sub> particles in the Fig. 12c, indicating that almost all Ge<sub>3</sub>N<sub>4</sub> transforms into Ge with the increase of MoO<sub>3</sub>. Here, the MoO<sub>3</sub> had been converted into Mo<sub>2</sub>N due to in the NH<sub>3</sub> flow at 800 °C (Fig. 5, 800 °C). Fig. 12 again demonstrates the process of Ge generation goes through two stages. Firstly, GeO<sub>2</sub> is reduced to Ge<sub>3</sub>N<sub>4</sub>, and then Ge<sub>3</sub>N<sub>4</sub> decomposed into Ge by the catalysis of Mo<sub>2</sub>N.

Fig. 13 shows the UV-vis diffuse reflectance spectra of MoO<sub>3</sub>/GeO<sub>2</sub> calcined in the NH<sub>3</sub> flow with different mass ratios of MoO<sub>3</sub>. The raw material of GeO<sub>2</sub> show a strong light absorption at ultraviolet region with the absorption edge of 218 nm, which means it is a large gap semiconductor. With the amount of MoO<sub>3</sub> increasing from 0 to 5.0%, the light absorption region gradually extends from ultraviolet region to visible region and the absorption strength gradually increases. The Ge prepared from 5.0% MoO<sub>3</sub>/GeO<sub>2</sub> shows the most strongest light absorption in the range from 200 nm to 800 nm. The light absorption curve of the Ge prepared in NH<sub>3</sub> flow is same as that prepared in H<sub>2</sub> flow except the absorption strength. The difference of absorption strength can be attributed to the small amount of Mo<sub>2</sub>N catalyst.

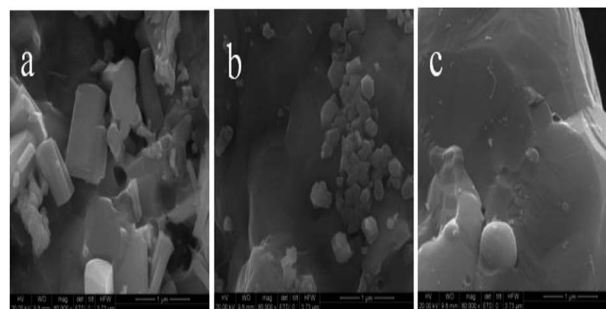


Fig. 12 SEM images of samples prepared in the NH<sub>3</sub> flow from 2.0% MoO<sub>3</sub>/GeO<sub>2</sub> at 800 °C for 0.5 h (a), 2.0% MoO<sub>3</sub>/GeO<sub>2</sub> at 800 °C for 2 h (b) 5% MoO<sub>3</sub>/GeO<sub>2</sub> at 800 °C for 2 h (c).



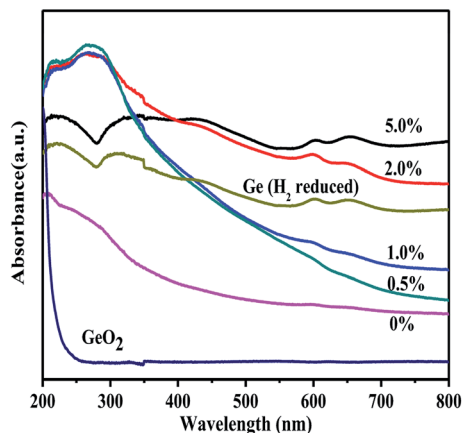


Fig. 13 The UV-visible diffuse reflectance spectra of  $\text{MoO}_3/\text{GeO}_2$  with different mass ratios of  $\text{MoO}_3$  calcined in  $\text{NH}_3$  flow at  $800^\circ\text{C}$  for 2 h. The spectra of  $\text{GeO}_2$  and Ge prepared in the  $\text{H}_2$  flow at  $650^\circ\text{C}$  for 4 h are presented for comparison.

## 4 Conclusions

A fast, low cost and safe method for the Ge synthesis has been reported by the  $\text{NH}_3$  reduction of  $\text{GeO}_2$  using a  $\text{Mo}_2\text{N}$  catalyst. When  $\text{GeO}_2$  and 5.0%  $\text{MoO}_3$  is mixed and nitrided in  $\text{NH}_3$  flow at  $800^\circ\text{C}$ , the Ge is formed in 10 min. The prepared Ge shows micron scale particles size and good light absorption both in the ultraviolet and visible region. The reaction mechanism of Ge generation carries out a two-stage process.  $\text{GeO}_2$  is converted into  $\text{Ge}_3\text{N}_4$  firstly, and then  $\text{Ge}_3\text{N}_4$  is decomposed into Ge with the  $\text{Mo}_2\text{N}$  catalyst.  $\text{Mo}_2\text{N}$  instead of  $\text{MoO}_3$  is demonstrated the catalyst for the Ge generation by two proofs. One is that  $\text{MoO}_3$  is converted into  $\text{Mo}_2\text{N}$  at  $800^\circ\text{C}$  in the  $\text{NH}_3$  flow. Another is that a small part of Ge is produced from both the mixed  $\text{Mo}_2\text{N}/\text{GeO}_2$  and the  $\text{Mo}_2\text{N}/\text{Ge}_3\text{N}_4$  calcined in  $\text{N}_2$  flow, whereas there is no Ge generated from both  $\text{MoO}_3/\text{GeO}_2$  and the  $\text{MoO}_3/\text{Ge}_3\text{N}_4$ . Finally, the method for Ge preparation in  $\text{NH}_3$  flow has been compared with the industrial method in  $\text{H}_2$  flow. Our presented method has the advantages of fast and safety and has great potential for industrialization. The proposed  $\text{Mo}_2\text{N}$  boosting the  $\text{Ge}_3\text{N}_4$  decomposition has guiding significance to other nitride decomposition system.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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